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Loontjens, Ton

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HIGHLIGHT

Modular Approach for Novel Nanostructered Polycondensates Enabled by the Unique Selectivity of Carbonyl Biscaprolactam

TON LOONTJENS
DSM Research, Performance Materials-Chemistry and Technology, P.O. Box 18, 6160MD Geleen, The Netherlands

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ABSTRACT: New enabling chemistries have been developed to produce novel well-defined polymeric materials through the additions of small amounts of reactive functional compounds to standard polymers during regular processing steps. We found that carbonyl biscaprolactam and its derivatives couple polymer chains in a strictly linear fashion. The requirements for fast and well-controlled coupling reactions, a prerequisite to apply this modular concept, were met. The breakthrough to produce a wide variety of novel polymers came when we found that many building blocks, provided with functional groups and blocked isocyanate groups, could be made on the basis of this chemistry. Blocked isocyanate groups are very suitable coupling units to fix desired functions onto polymer backbones. In one example, antifouling coatings were prepared by introducing fluorine groups. In another case, blocked isocyanate functional acrylates were built into a polyacrylate to make self-crosslinkable coatings. In another illustration, the concept was demonstrated by a novel route to prepare polyrotaxanes from rotaxane monomers provided with blocked isocyanates as polymerizable stopper groups. These reactive functional compounds gave, in a controlled manner, polymeric materials with substantially improved properties. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 3198–3205, 2003

Keywords: chain extension; carbonyl biscaprolactam; functionalization of polymers; reactive extrusion; coatings; blocked isocyanates

TON LOONTJENS

Ton Loontjens (18-05-45) is the Principal Scientist of Macroorganic Chemistry at DSM Research in Geleen, the Netherlands. His primary responsibility is to search for new opportunities in performance materials in academia, in conferences, and so forth and to translate them into industrial projects. Current topics of interest are reactive processing (chain extension), coatings (crosslinking), the introduction of functional groups into regular polymers, and nanostructured materials.

After his study in organic chemistry, Loontjens started at DSM Research in 1975 as the leader of the propylene polymerization group. In 1980 he became work-group leader of polyethylene and construction resins. From 1985 until 1992, he was head of a polymer chemistry department on coating resins, melamine resins, and stabilization of polymers.

Correspondence to: T. Loontjens (E-mail: ton.loontjens@dsm.com)

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He then became head of a polymer chemistry department on polyesters, nylons, and coatings. Since 1995, he has held the position of Principal Scientist. Loontjens is coauthor of more than 35 scientific articles and more than 50 patents.

INTRODUCTION

In the 1970s, a number of new high-heat resins were commercially launched such as liquid crystalline polymers (LCPs), polysulfones, polyimides, poly(ether imide)s, and aromatic polyamides. It was anticipated that the market for these materials would become a major one; however (although successful), the market share of these polymers is still relatively small. After this initial flood of new products on the market, hardly any new polymer was introduced on the kiloton scale. It became clear that the additional added value of most of the new polymers was not sufficient to persuade companies to invest in these developments, despite the continuous request from the market for improved properties.

When realizing this, we came to the conclusion that new routes had to be followed that were based on existing polymers and existing processing technologies.

The preparation of modified polymers from regular polymers by reactive extrusion is well known. The chemistry that has been used up until now is (unfortunately) ill defined and only acceptable when mixtures of polymers are allowed.

A prerequisite to produce well-defined polymers by reactive extrusion is that the applied chemistry has to be fast and well controlled. This is very demanding because the processing conditions are quite violent (the temperature range is 250–300 °C, and the residence time is only a few minutes).

Many polymers, in particular polycondensates, have —OH, —NH_2, or —COOH functional end groups, and although they do have the ability to react in reactive extrusion processes, no appropriate chemistry has been found. New coupling routes had to be located, but they would only be recognized as real breakthroughs if they were able to produce polymers with substantial improved properties.

Numerous chemicals have been described for this purpose, but until now hardly any have given acceptable results. For instance, diphenyl carbonate,[1] aliphatic and aromatic bisoxazolines,[2–11] bisepoxies,[12,13] diisocyanates,[14–16] phosphites,[17–19] the triscaprolactamate of phosphorous acid,[20,21] bisketenimines,[22] and dianhydrides[23] have been reported, but none of them are really successful (because of branching, slow reaction rates, high toxicity, discoloration, etc.). From these, aromatic bislactams[24,25] are one of the best candidates and therefore a good starting point for us to investigate their scope and limitations.

Here, we report an enabling chemical technology to increase the molecular weight of regular polymers under regular processing conditions in a strictly linear way. Furthermore, we discuss our modular approach in which coupling agents, provided with various functional groups, give substantial improvements of the polymeric properties.

MODULAR APPROACH

The concept of the modular approach (as depicted in Fig. 1) is in principle quite simple. Functional chain extenders introduce novel properties by reacting with the end groups of polycondensates in a regular processing step. The key issue, to make a modular approach viable, is to find the fast and clean chemistry. The first step toward this challenging target is to develop chemical reactions that couple polymer chains in a strictly linear and controllable fashion. Only after complete control of these reactions had been achieved were we able to use this chemistry as a vehicle to introduce special functional groups.

CHAIN EXTENSION

Mechanical properties of polymers increase by enhancing the molecular weight. Because polycondensates are prepared in bulk, their viscosity will limit their attainable molecular weight. Above a certain level, the viscosity

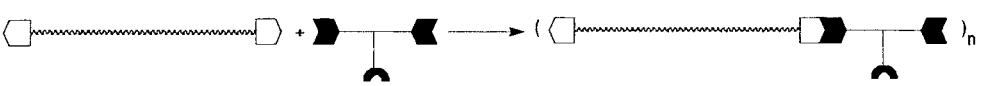


Figure 1. Introduction of functional groups in polycondensates during reactive extrusion by a modular approach.

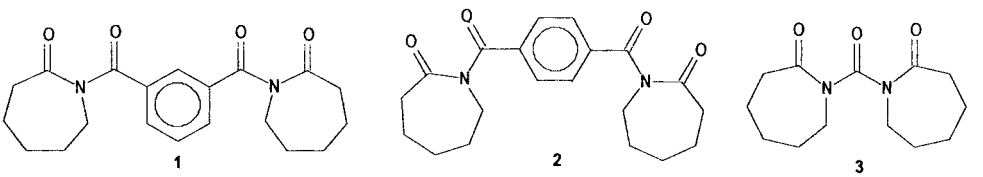


Figure 2. Bislactams from diacids and caprolactam: **1**, isophthalic acid; **2**, terephthalic acid; and **3**, carbonic acid.

will become too high to empty a reactor in a reasonable time. Higher molecular weight polymers have to be prepared by solid-state postcondensation (SSP), whereby polymers are heated for 20–50 h at 200 °C *in vacuo*. This is a laborious and expensive method, and chemical routes that can replace this process step will be highly accepted. As previously mentioned, and also confirmed by us, some researchers have demonstrated that *N*-acyllactames are suitable chain extenders.[26] In nearly all cases, the *N*-acyllactams were prepared from caprolactam and the acid chloride of iso- or terephthalic acid (**1** and **2**, respectively, Fig. 2). Although the results were promising, none of these products reached commercial status. Convinced of the opportunities, we investigated carbonyl biscaprolactam [**3** in Fig. 2, carbonyl biscaprolactam (CBC), ALLINCO] on the basis of caprolactam and phosgene, the cheapest acid chloride available. An additional advantage of this bislactam is that only small amounts of this chemical would be needed because of its low molecular weight.

We have found that CBC is very effective in enhancing the viscosity of polycondensates, such as poly(ethylene terephthalate) (PET), poly(1,4-butylene terphthalate) (PBT), nylon-6, nylon-4,6, and nylon-6,6 (Fig. 3 provides more detailed results with respect to PET and nylon-6).[27] The viscosity of the polymers is increased in a controlled way, independent of the starting level of the viscosity. Moreover, CBC (supplied by DSM) is nontoxic.

Chain extension with CBC affords the same increase in viscosity in only a few minutes as solid-state postcondensation does in 20–50 h at 200 °C. The size exclusion chromatography (SEC) data and rheology measurements showed that the polymers were strictly linear; thus, no branching was observed. Therefore, the challenging step, coupling regular polymers in a controlled manner during regular processing, was successfully achieved.

The successful use of this technology, to modify the properties of conventional polymers, sets the scene for the next steps in which we attempted to modify polymers with functional reactive additives. This is first demonstrated by two examples with coatings and then later with polymers. In both cases, novel blocked isocyanates (BIs) were used that could only be prepared because of the unique properties of CBC. The scope and limitations of this methodology are described first.

FUNCTIONAL BLOCKED ISOCYANATES

The chain extension of polycondensates with CBC was done at temperatures well above 200 °C. Under those

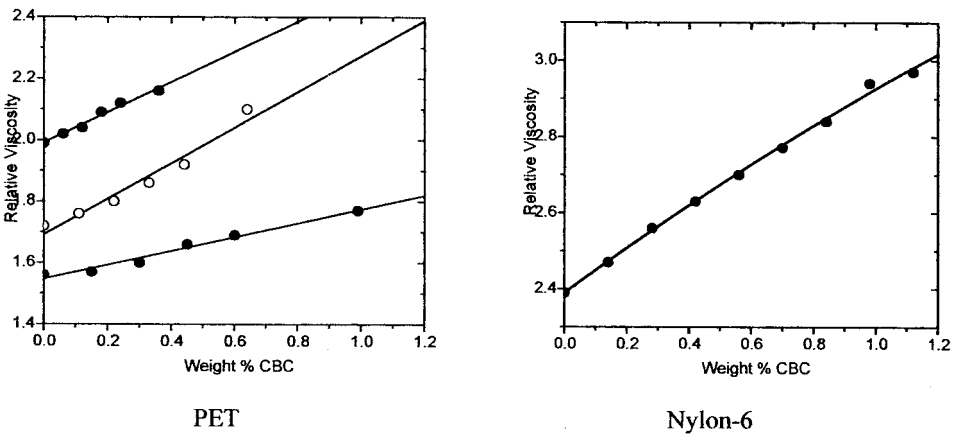
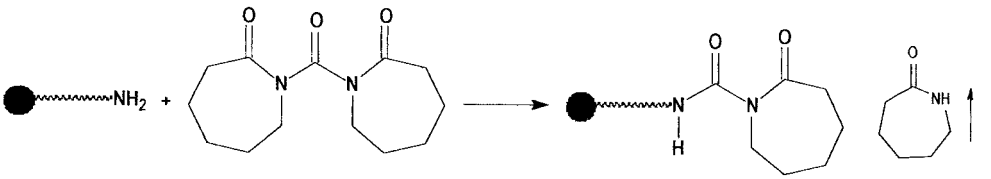


Figure 3. Increase of viscosities of PET and nylon-6 with an increasing amount of CBC (T = 280 °C for PET and 240 for nylon-6; the residence time is 4 min).



Scheme 1. Preparation of BIs from amines and CBC.

conditions, one molecule of CBC couples two hydroxy or amino groups in two consecutive steps. If it were possible to stop the reaction halfway through, for example, at lower temperatures, then numerous interesting reactive compounds could be made. To our great pleasure, we found that the reaction does indeed stop halfway, at a temperature of about 100 °C. Even more exciting was the fact that amines react with CBC in a very selective way, yielding BIs in an almost quantitative yield (see Scheme 1). It appeared that CBC has a unique property to make BIs without any side products, in a one-step reaction.

Various BIs were subsequently prepared by reacting stoichiometric amounts of CBC and amines for 2 h, in toluene at 100 °C. Although amines do react with BIs at elevated temperatures, they do not do this at 100 °C.

An extreme selectivity is found when CBC reacts with compounds comprising both primary and secondary amines. In this case, the primary amines react exclusively with CBC (again almost quantitatively), leaving the secondary amine available for further elaboration. This is quite astounding if one considers that now two selectivities have to be fulfilled, that is, substitution of only one of the two caprolactam rings and reaction only with primary amines. For example, bishexamethylene triamine reacts exclusively via the primary amino groups with no indication that the secondary amine also reacts. Similar surprising results were obtained with amines that comprised hydroxy groups. In this case, only the amino groups react (with a very high selectivity), leaving the hydroxy group available for further functionalization. For instance, propanol amine reacts quantitatively with equimolar amounts of CBC to produce the caprolactam-blocked γ-hydroxy-propyl isocyanate. The hydroxy groups are available for further elaboration.

The synthesis of BIs from alcohols is unprecedented. However, we found that alcohols do react with CBC to give BIs in high yields, whereby because of the ring opening of one of the caprolactam rings, BIs are formed in which the nitrogen of the isocyanate originates from caprolactam. The addition of a catalyst (e.g., $MgBr_2$)[28] results in a completely different reaction pathway from what is observed with amines. The yield of BIs, which was about 90%, was slightly less than CBC reactions with amines. However, because alcohols are more abundantly available and cheaper than amines, this method is also very valuable. For example, a four-functional BI was prepared in high yields from pentaerytritol. It was, to the best of our knowledge, the first time that BIs were prepared from alcohols.

The preparation of BIs from amines containing secondary amino or hydroxy groups enables us to introduce other functionalities. It is an indispensable condition for our modular concept that the (functional) BIs give the same (clean and fast) chain-extension reactions, as CBC does. Although BIs are well known in coating applications, they have not been described as chain extenders. Fortunately, we have found[29–33] that they do indeed exhibit the same excellent chain-extender behavior as CBC. With this in mind, we now have all the necessary tools to introduce functional groups into polymers and coatings. Numerous examples of amine or hydroxy functional BIs were prepared, and a few representative examples are illustrated in Figure 4. These compounds could not be synthesized via the common isocyanate route because the isocyanates would react immediately with the active hydrogen.

COATINGS

BIs have been used frequently in coating applications.[34–38] The only purpose of these additives is to crosslink the coating resin. It is a disadvantage that the

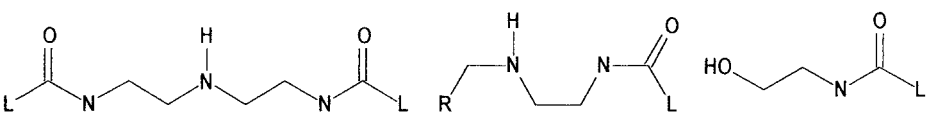
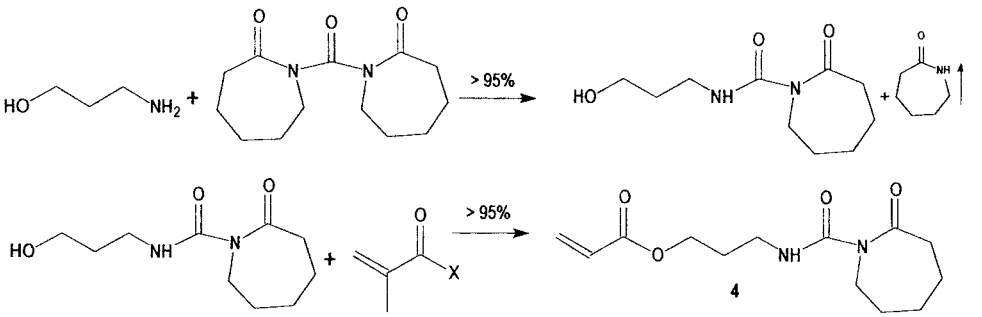


Figure 4. BIs prepared from CBC containing a secondary amine of a hydroxy group enabling further functionalization (L: caprolactam).



Scheme 2. Synthesis of caprolactam-blocked 2-methacyloxyoxypropyl isocyanate.

crosslinker has to be added in a separate compounding step (costs), which is now common practice.

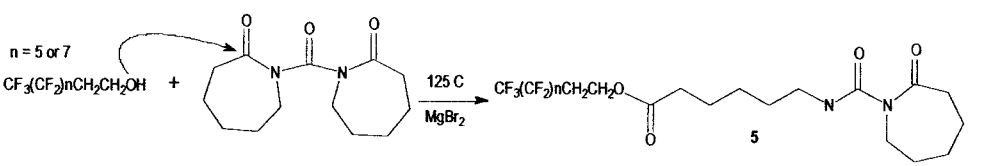
Here we report the preparation of self-crosslinkable coatings on the basis of our new technology. In this case, there is no need for an additional compounding step because the crosslinker is built in during the polymerization. Polymethacrylate resins were prepared by the radical polymerization of methyl methacrylate, hydroxyethyl methacrylate (HEMA), and a new monomer that contains (besides the methacrylate group) a BI moiety. The synthesis of this monomer 4 is shown in Scheme 2.

The reaction between γ-aminopropanol and CBC proceeds in near-quantitative yields. From ^{1}H NMR, we saw that only the amino group reacts with CBC, and there is no indication that the hydroxy group reacts. The hydroxy functional BIs are converted into a methacrylate by reacting it with methacryloyl chloride. Polymerization of the methacrylate monomers proceeded in toluene at a temperature of 120 °C with azobisisobutyronitrile as a radical initiator. The molecular weights (from SEC data based on polystyrene standards) were about 4000 D. Coating resins, with 10 mol % of HEMA and 10 mol % of monomer 4, were cured for 20 min in a gradient oven (temperature range: 150–250 °C). At a curing temperature of 170 °C or higher, coatings were obtained that had a very high solvent resistance (>300 acetone double rubs). The significance of this method is that coating resins are produced, whereas no compounding step is needed to introduce crosslinkers. This example suggests that special features were obtained with mostly standard monomers in a regular processing step, through adding small amounts of novel species with unique properties.

Another example of the use of CBC to make functional materials was to prepare antifouling coatings. In this investigation (in cooperation with W. Ming, University of Eindhoven),[39] novel fluorine-containing BIs were prepared with our methodology (as depicted in Scheme 3).

In this case, the BIs were made directly from an alcohol. As far as we are aware, it is not possible to do this in another way, in a one-step reaction.

Hydroxy functional polyester resins, trifunctional BIs, and various amounts of monomer 5 were used to make a number of clear coats. As a result of its low surface energy, monomer 5 migrated to the surface, enriching the surface with fluorine. As expected, there is competition between the diffusion of the fluorinated BI to the surface and the coupling of the isocyanate units to the hydroxy groups of the polyester. For instance, the surface enrichment was greater when a cure temperature of 150 °C was used as compared with a cure temperature of 200 °C. However, in both cases the fluorine content of the surface was about 20–50 times higher than in the bulk, as measured by X-ray photoelectron spectroscopy. We have made coatings with less than 4 wt % of fluorine with a surface tension value (10 mN/m) lower than Teflon (20 mN/m, 76 wt % F). Antifouling properties, which are expected to correlate with surface tensions, will be measured in the near future. In this example, substantially improved properties of coatings can be obtained from standard resins under regular processing conditions by adding small amounts of additives with special properties.



Scheme 3. Preparation of a fluorine-containing BI.

POLYROTAXANES

To illustrate the methodology in polymers, we designed a new way to make polyrotaxanes on the basis of standard starting materials. Rotaxanes are compounds whereby a macrocyclic component circumscribes a linear thread molecule on which the macrocycle is not covalently attached to the thread and is therefore allowed to move freely up and down the thread.[40] Bulky stopper groups at either end of the thread provide enough steric hindrance to prevent the macrocycle from falling off and dethreading. The synthesis of true polyrotaxanes is even more complicated because of the need to incorporate polymerizable groups onto the monomer rotaxane while still maintaining its unique structure. Until now, three of the following major strategies have been developed toward the synthesis of these materials:

1. A preformed polymer is dissolved in (a solution of a) macrocycle that, over time, threads onto the polymer chain forming pseudo-polyrotaxanes.[41–43] The macrocycle is free to thread or dethread from the polymer chain at any time resulting in an unstable polyrotaxane species, hence the use of the term pseudo.
2. Polymerization of the thread occurs in the presence of the macrocycle. This strategy again results in unstable pseudo-polyrotaxanes as the macrocycles are free to dethread both from the monomer before polymerization but also from the polymer chain itself.
3. Polymerization is done in the presence of a macrocycle with monomers that contain bulky blocking groups that prevent the macrocycle from falling off the newly formed polymer chain.

In all these cases, threading of the macrocycle onto the (growing) polymer chain is done in an entirely reversible manner, which inevitably leads to difficulties in controlling the amount of threaded macrocycle in the polymer. With the methodology developed for the chain extenders, we successfully managed to synthesize a series of stable monomer rotaxanes bearing bulky stoppers possessing BI groups synthesized from CBC. By varying the number and location of these BI stopper groups, we were able to synthesize three different rotaxane monomers that, when mixed at temperatures of around 180 °C with an α,ω-amino-functionalized oligomer in the bulk, produced stable main-chain, side-chain, and crosslinked polyrotaxane topologies (Fig. 5).

This represents a new strategic tool in the fabrication of such novel macromolecular architectures. To the best

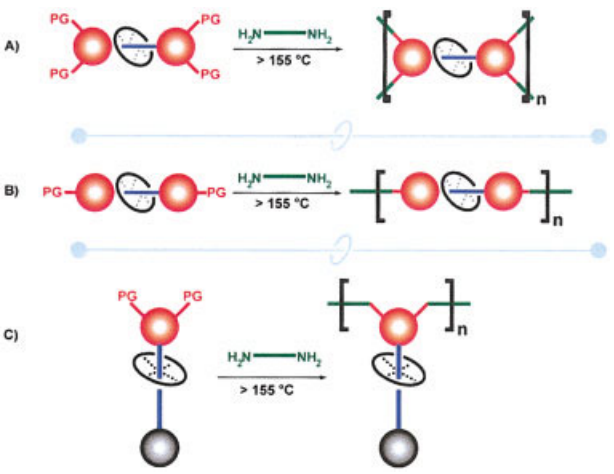
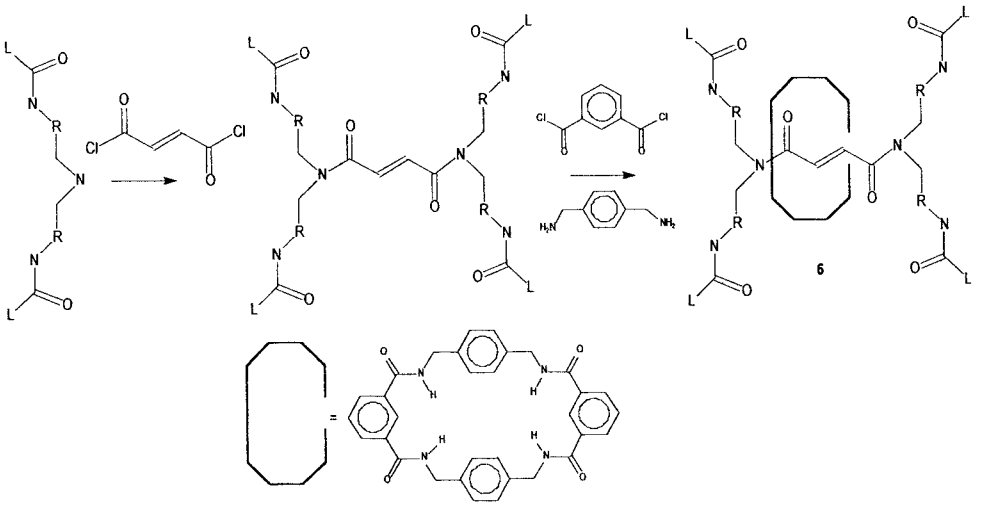


Figure 5. Novel strategy to make well-defined polyurea rotaxanes; PG are polymerizable groups (BIs), and the amines are Jeff amines.

of our knowledge, it is the first example of a stable rotaxane monomer that was produced that contained polymerizable bulky stopper groups. For the purpose of this article, we only discuss the synthesis of rotaxane monomer A; a more detailed description of this work is given elsewhere.[44]

We synthesized the tetra-BI thread molecule (Scheme 4) with the fumaryl template described by Gatti et al.,[45] (which affords high yields of rotaxanes) through the condensation of fumaroyl chloride and the free secondary amine of the di-BI (synthesized from the reaction of bishexamethylene triamine with CBC, as mentioned previously). Slow addition of separate dilute solutions of xylylene diamine and isophthalloyl chloride in chloroform to a stirred solution of the tetra-BI thread (also in chloroform and in the presence of a base) afforded the tetra-BI rotaxane monomer in 70% yield. Subsequent polymerization of the tetra-BI rotaxane monomers A by heating them with a number of different diamines [e.g., Jeffamine D400, an α-ω-functional poly(propylene glycol) with a number-average molecular weight of ~400 D] to temperatures of around 180 °C produced rubbery materials with a typical modulus of about 2 MPa and an elongation at break of >100%. ^{1}H NMR of a swollen sample of this polyrotaxane in deuterated chloroform confirmed the presence of the rotaxane subunits as an integral part of the polymer material. With this novel technology of selectively forming BIs from amines with CBC, we have been able to synthesize the first examples of stable rotaxane (functional) building blocks that can be used as chain extenders for commercial polymer materials, thus providing these materials with enhanced properties and perhaps added value.



Scheme 4. Preparation of the rotaxane monomer A (L: caprolactam).

CONCLUSIONS

We have described a novel method to produce polymer with special properties with a modular approach on the basis of a new, reactive chemical, CBC (ALLINCO). Standard polymers can be modified in a controlled manner with (functional) reactive compounds, under regular processing conditions. We have demonstrated that the molecular weight of polycondensates can be raised in a strictly linear way through chain extension, giving (in a simple way) a substantial improvement of the mechanical properties. This process can and will replace the laborious SSP.

Additionally, we have developed a new method in which BIs can be made in high yields directly from amines and CBC without the need of specialized equipment or hazardous chemicals. Moreover, BIs can be prepared directly form alcohols and CBC, which is an unprecedented result. Furthermore, BIs were prepared containing secondary amine or hydroxy groups, thus allowing further elaboration. In this respect, we have demonstrated many examples whereby we have attached functionality to these molecules to produce self-crosslinkable coatings or antifouling coatings with high solvent resistance or surface tensions lower than Teflon, respectively. Finally, we have demonstrated that the sky is the limit regarding the choice of functionality that we can incorporate into these molecules. Even complex molecules such as rotaxanes have successfully been incorporated into polymers to produce a new breed of polyrotaxanes, thanks to the selectivity and reactivity of CBC.

The author acknowledges DSM for allowing him to perform this work and to publish it. In addition, the author acknowledges the contribution of many colleagues, particularly B. Plum, A. Nijenhuis and B. Scholtens (DSM), W. Ming (University of Eindhoven), R. Mülhaupt and S. Maier (University of Freiburg), and D. Leigh (University of Edinburgh). The author thanks T. Kidd for his contribution and for his support toward this publication.

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